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Octahedral Chromium(III) Complexes in Dipolar Aprotic Solvents. IV*. Isomerization and Solvolysis Reactions of *cis* and *trans*-$[CrBr_2(en)_2]^+$ in Anhydrous Dimethyl Sulphoxide

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The reaction of cis and trans–$[CrBr_2(en)_2]^+$ in dimethyl sulphoxide (DMSO) have been studied over a range of temperature and supporting bromide ion concentrations. The equilibrium solutions are dominated by the species cis–$[Cr(DMSO)_2(en)_2]^{3+}$ and cis–$[CrBr(DMSO)(en)_2]^{2+}$. These species have been isolated and characterized as have the thermodynamically less stable species trans–$[Cr(DMSO)_2(en)_2]^{3+}$ and trans–$[CrBr(DMSO)(en)_2]^{2+}$. The kinetics of all possible isomerization, solvolysis and anation reactions have been studied, and are found to be of a dissociative type with pronounced effects due to ion association.

Introduction

A number of studies have been made of cobalt (III)[1-5] and chromium (III)[6-9] bisethylenediamine–complexes in dipolar aprotic solvents using a range of anionic nucleophiles and solvents showing a range of coordinating power. To date the systems investigated have been dominated at equilibrium by complexes containing one or more anionic ligands. Chromium (III) shows a greater tendency to coordinate DMSO than cobalt (III), and the solvolysis of complexes containing anionic ligands is more pronounced for more polarizable ligands. These results led us to study the present system in the hope that the reactions of the full range of complexes *cis* and *trans*-$[CrBr_2(en)_2]^+$, *cis* and *trans*–$[CrBr(DMSO)(en)_2]^{2+}$ and *cis* and *trans*–$[Cr(DMSO)_2(en)_2]^{3+}$ could be followed. This has proven to be correct and all the substitution processes of these complexes, except exchange of bromide for bromide and DMSO for DMSO exchange data, which in the cobalt (III) system was measured using D_6–DMSO and proton resonance spectroscopy,[10,11] could not be obtained here for the paramagnetic chromium (III) system.

Experimental

(1) *Preparation of Complexes.* (a) *cis*–dibromobisethylenediaminechromium(III) salts, *bromide monohydrate.* This salt was synthesized by standard techniques[12,13]. Recrystallization was effected from a 0.5M hydrobromic acid solution at room temperature by the addition of sodium bromide. After washing with ethanol and ether the complex was dried at 110° for 4 hours. This drying procedure also served to convert any *cis*–$[CrBr(H_2O)(en)_2]Br_2$ contamination to the dibromo salt. *Anal.* calcd for *cis*–$[CrBr_2(en)_2]Br.H_2O$: C, 11.2; H, 4.2; N, 13.0; Br, 55.8. found: C, 11.1; H, 4.2; N, 13.0; Br, 55.4. *perchlorate.* This salt was prepared from the recrystallized bromide salt and purified by the method of Quinn and Garner[12]. The dark purple crystals were vacuum dried for 48 hours. *Anal.* calcd for *cis*–$[CrBr_2(en)_2]ClO_4$: Br, 37.0. found: Br, 36.9.

(b) *trans*–dibromobisethylenediaminechromium (III) salts, *bromide monohydrate.* Initially a modified version[12] of Pfeiffer's method[14] was used to synthesize this salt. Subsequently the method of Vaughn et al.[15] was used exclusively. The crude salt was recrystallized twice by dissolving it in 0.1M hydrobromic acid and cooling the solution in ice. Alcoholic hydrogen bromide was added slowly with stirring. The bright green precipitate was filtered and washed with ethanol and ether, then vacuum dried for 18 hours. *Anal.* calcd for *trans*–$[CrBr_2(en)_2]Br.H_2O$: Br, 55.8. Found: Br, 55.5. *perchlorate.* This salt was prepared by the dropwise addition of 70% per-

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chloric acid to an aqueous solution of the bromide salt. The precipitate was recrystallized twice by dissolving it in DMSO at room temperature and adding ice-cold 10% perchloric acid. The green crystals were filtered and washed with water, followed by ethanol and ether, and vacuum dried for 48 hours. *Anal.* calcd for *trans*–$[CrBr_2(en)_2]ClO_4$: C, 11.1; H, 3.7; N, 13.0; Br, 37.0. found: C, 11.7; H, 3.8; N, 12.6; Br, 36.9.

(c) *cis*-bromo(dimethyl sulphoxide)bisethylenediaminechromium(III) perchlorate.

Although the preparation of this complex involves essentially the same method used for similar complexes,[16,17] a number of modifications have been made to the established technique. *Cis*–$[CrBr_2(en)_2]ClO_4$ was dissolved in a minimum volume of DMSO at room temperature and an equimolar, saturated solution of silver perchlorate in DMSO was added slowly with stirring. The mixture was left for 3-4 hours in the dark. After filtering, a five fold excess of ethanol was added to the filtrate followed by a sufficient volume of ether to form an oil. The supernatant liquid was decanted off and an ice-cold, saturated aqueous solution of lithium perchlorate added slowly with vigorous stirring. The resulting red crystals were recrystallized twice from water, then washed with ethanol and ether, and vacuum dried for 48 hours. In the latter part of this research the nitrate perchlorate salt was prepared with a greater yield. *Anal.* Calcd for *cis*–$[CrBr(DMSO)(en)_2](ClO_4)_2$: C, 13.6; H, 4.2; N, 10.6; Br, 15.1. Found: C, 13.6; H, 4.4; N, 10.6; Br, 15.3.

(d) *Cis*-di(dimethyl sulphoxide)bisethylenediaminechromium(III) perchlorate.

The preparation of this complex is similar to the synthesis described directly above with the exception that two moles of silver perchlorate were added for each mole of *cis*–$[CrBr_2(en)_2]ClO_4$. *Anal.* Calcd for *cis*–$[Cr(DMSO)_2(en)_2](ClO_4)_3$: C, 15.2; H, 4.5; N, 8.9; S, 10.2. Found: C, 15.4; H, 4.7; N, 8.7; S, 10.0.

(e) *Trans*-bromo(dimethyl sulphoxide)bisethylenediaminechromium(III) perchlorate.

Equimolar solutions of *trans*–$[CrBr_2(en)_2]ClO_4$ and silver perchlorate in DMSO were mixed and allowed to digest for two hours at room temperature in the dark. After filtering off the silver chloride, three volumes of ethanol and one volume of ether were added and the mixture cooled on ice for 15 minutes. The gelatinous grey-green precipitate was filtered off and recrystallized three times from water. The pure complex was washed with ethanol and ether and vacuum dried at 50° for 48 hours. *Anal.* Calcd for *trans*–$[CrBr(DMSO)(en)_2](ClO_4)_2$: C, 13.6; H, 4.2; N, 10.6; S, 6.1; Br, 15.1. Found: C, 13.7; H, 4.3; N, 10.3; S, 5.7; Br, 15.1.

(f) *Trans*-di(dimethyl sulphoxide)bisethylenediaminechromium(III) perchlorate

This complex was originally prepared by Fee, Harrowfield and Jackson[9] by the method described above using twice the amount of silver perchlorate. Despite the precaution taken of storing the fawn crystals in the dark they began to noticeably decompose after approximately 3 weeks. *Anal.* Calcd for *trans*–$[Cr(DMSO)_2(en)_2](ClO_4)_3$: C, 14.8; H, 4.7; N, 8.6; S, 9.9. Found: C, 14.8; H, 4.8; N, 8.3; S, 9.9.

(2) *Other Reagents.* Tetra-n-butylammonium bromide (Eastman Organic Chemicals) was dried overnight by vacuum desiccation over anhydrous magnesium perchlorate.

The dimethyl sulphoxide was purified and dried as previously. The solvent was stored in the dark and was never used more than five days after the final fractionation.

(3) *Experimental Technique.* Spectrophotometric results were collected on either a Beckman D.U. spectrophotometer or an automatic Perkin Elmer 450 double beam spectrophotometer. The kinetic runs were followed in stoppered absorption cells in thermostatted cell blocks. Pure component spectra were measured at all temperatures at which analysis was carried out and in Figure 1 are presented for 22°. Precautions were taken at all times to exclude water.

The rate constants were calculated by normal methods using optical densities directly. The rate constants presented here are initial first order rate constants, calculated on the assumption of the total removal of the reactant. For the majority of reactions good first order plots were found for at least one half-life indicating that the reverse reaction did not interfere in the initial stages. In some cases a subsequent reaction was found to occur and these cases were treated as a normal case of subsequent first order processes. The rate constants were obtained by using a computer program for line of best fit, as were activation energies.

The maximum overall error in the rate constants is ±4% and the values were reproducible to ±2%.

Results

(1) *Equilibrium Studies.* Reproducible equilibrium results were obtained and the equilibrium product distribution was independent of the starting materials which in these experiments was usually *cis*–$[Cr(DMSO)_2(en)_2](ClO_4)_3$ and $(n\text{-}Bu)_4NBr$ although the *cis*- and *trans*–$[CrBr_2(en)_2]^+$, *cis* and *trans*–$[CrBr(DMSO)(en)_2]^{2+}$ and *trans*–$[Cr(DMSO)_2(en)_2]^{3+}$ cations were all used. More than 98% of the equilibrium system was described by the equation:

$$\textit{cis}\text{–}[CrBr(DMSO)(en)_2]^{2+} + DMSO = \textit{cis}\text{–}[Cr(DMSO)_2(en)_2]^{3+} + Br^- \qquad (1)$$

over an uncoordinated bromide concentration range from $0–82 \times 10^{-3}\,M$ with a total complex concentration of $3.95–4.35 \times 10^{-3}\,M$. Some *trans*–$[Cr(DMSO)_2(en)_2]^{3+}$ ion was present at low bromide concentrations ($< 15 \times 10^{-3}\,M$) but this species was never more than 2% of the total complex concentration. The equilibrium product distribution is presented in Figure 2 as a function of uncoordinated bromide ion

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concentration. These results come from a combination of spectrophotometric complex analysis backed by potentiometric bromide determinations.

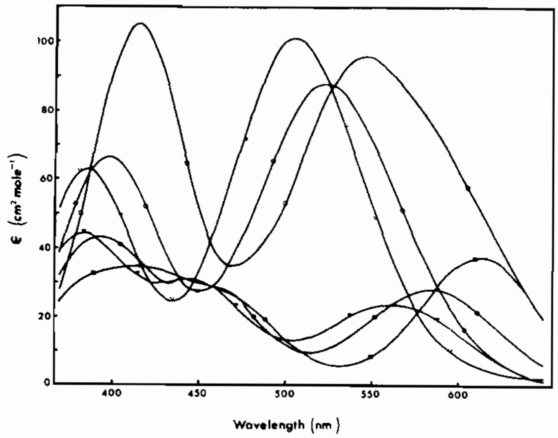

Figure 1. Spectra of Component Complex Ions.

- □ cis-$[CrBr_2(en)_2]^+$
- ○ cis-$[CrBr(DMSO)(en)_2]^{2+}$
- △ cis-$[Cr(DMSO)_2(en)_2]^{3+}$
- ■ trans-$[CrBr_2(en)_2]^+$
- ● trans-$[CrBr(DMSO)(en)_2]^{2+}$
- ▼ trans-$[Cr(DMSO)_2(en)_2]^{3+}$

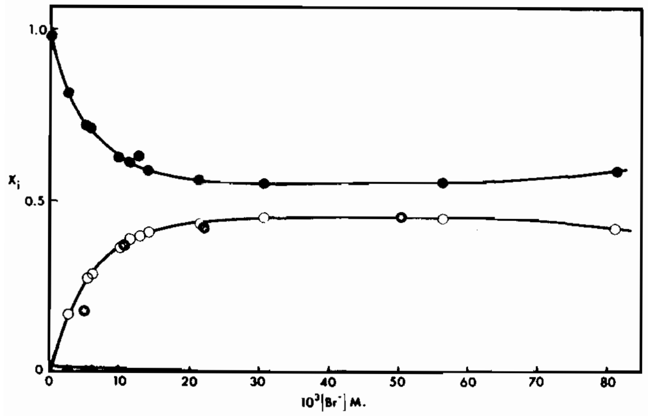

Figure 2. Equilibrium Composition as a Function of Uncomplexed Bromide Ion Concentration.

- ● cis-$[Cr(DMSO)_2(en)_2]^{3+}$ } Photometric Results
- ○ cis-$[CrBr(DMSO)(en)_2]^{2+}$ } Photometric Results
- ▲ trans-$[Cr(DMSO)_2(en)_2]^{3+}$ } Photometric Results
- ★ Potentiometric Results.

X_i presents the fractional composition of the Complex System

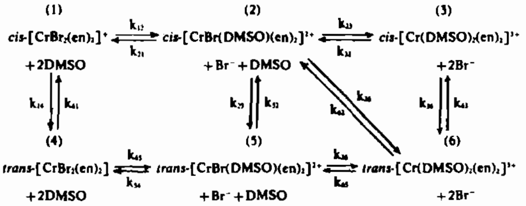

Figure 3. Complex Reaction Sequence.

(2) *Kinetic Results.* The kinetically significant paths are shown in Figure 3, which also defines the system of designating the rate constants for the system.

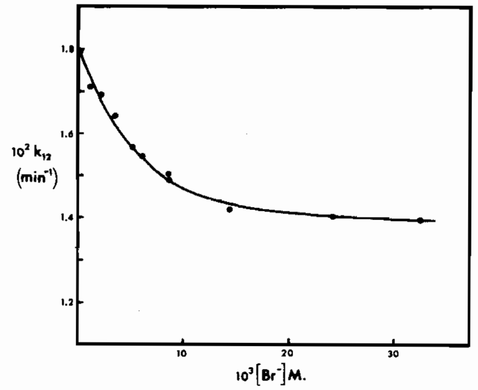

Figure 4. Variation of k_{12} with Uncomplexed Bromide Ion Concentration.

Figure 4 shows the rate constants for the solvolysis of cis–$[CrBr_2(en)_2]^+$, k_{12}, as a function of initial bromide concentrations at 50°C. Neither of the species trans–$[CrBr_2(en)_2]^+$ nor trans–$[CrBr(DMSO)(en)_2]^{2+}$ could be detected in the reaction mixtures and thus k_{14} and k_{15} are effectively zero.

The rate of solvolysis of trans–$[CrBr_2(en)_2]^+$, k_{45}, was bromide concentration independent (Table I) and resulted in total retention (k_{41} and k_{42} effectively zero).

The rates of removal of cis–$[CrBr(DMSO)(en)_2]^{2+}$ ($k_{23}+k_{26}$) were studied at 40°. Although no direct isomerization was observed ($k_{25}=0$), the appearance of some trans–$[Cr(DMSO)_2(en)_2]^{3+}$ at low bromide ion concentrations could not be immediately assigned to either a direct path, k_{26}, or to an indirect path (k_{23} followed by k_{36}). Subsequent study of the reactions of trans–$[Cr(DMSO)_2(en)_2]^{3+}$ indicated that k_{26} did exist. The values of ($k_{23}+k_{26}$) presented in Figure 5 as a function of initial bromide concentration are predominantly k_{23}, probably $>95\%$.

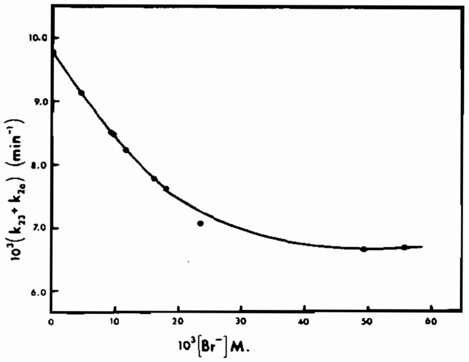

Figure 5. Variation of ($k_{23}+k_{26}$) with Uncomplexed Bromide Ion Concentration.

Trans–$[CrBr(DMSO)(en)_2]^{2+}$ was found to isomerize totally to cis–$[CrBr(DMSO)(en)_2]^{2+}$ even at zero

Table I. Rate Constants for Solvolysis of *trans*–$[CrBr_2(en)_2]^+$ in DMSO. Complex concentration: 4.93 – 5.05 × $10^{-3}M$

$10^3[Br^-]$ mol $l.^{-1}$	10^2k_{45} min^{-1}	Temp. °C	$10^3[Br^-]$ mol $l.^{-1}$	10^2k_{45} min^{-1}	Temp. °C
0	1.47	40.0	52.7	1.44	40.0
5	1.45	40.0	0	1.04	37.0
11.3	1.45	40.0	0	0.33	27.4
18.1	1.48	40.0	55.9	2.85	46.0
27.5	1.47	40.0	55.9	0.56	31.8
40.1	1.46	40.0	55.9	0.48	30.8

Table II. Rate Constants for the Isomerization of *trans*-$[CrBr(DMSO)(en)_2]^{2+}$ in DMSO. Complex concentrations: 4.85 – 4.95 × $10^{-3}M$

$10^3[Br^-]$ mol $l.^{-1}$	10^3k_{52} min^{-1}	Temp. °C	$10^3[Br^-]$ mol $l.^{-1}$	10^3k_{52} min^{-1}	Temp. °C
0	2.91	50.0	81.5	2.99	50.0
4.50	2.87	50.0	0	13.2	63.4
9.18	2.98	50.0	0	0.87	40.0
11.4	2.92	50.0	50.9	13.3	63.5
31.1	2.93	50.0	50.9	6.52	57.5
37.4	2.95	50.0	50.9	0.87	40.0
50.9	2.96	50.0			

Table III. Activation Parameters for the $[CrBr_2(en)_2]$ System. Bromide concentration is given in mol $l.^{-1}$; the enthalpy of activation, $\Delta H^{\circ *}$, in kJ mol^{-1}; and the entropy of activation, $\Delta S^{\circ *}$, in J $K^{-1}mol^{-1}$.

Complex	Rate Constant	$10^3[Br^-]$	$\Delta H^{\circ *}$ at 40°	$\Delta S^{\circ *}$ at 40°
cis-$[CrBr_2(en)_2]^+$	k_{12}	0	86±2	—37
		24.5	88±2	—32
trans-$[CrBr_2(en)_2]^+$	k_{45}	0	92±1	—20
		55.9	92±1	—20
cis-$[CrBr(DMSO)(en)_2]^{2+}$	k_{23}	0	80±1	—53
		49.9	81±2	—53
trans-$[CrBr(DMSO)(en)_2]^{2+}$	k_{52}	0	97±2	—29
		50.9	97±2	—28
cis-$[Cr(DMSO)_2(en)_2]^{3+}$	k_{32}	44.7	124±3	+75
trans-$[Cr(DMSO)_2(en)_2]^{3+}$	k_{63}	0	92±2	—40
	$k_{63}+k_{62}$	28.4	93±2	—31
	k_{62}	28.4	113±3	+25

bromide ion concentration. These rate constants (k_{52}), given in Table II, show little dependence on bromide concentration.

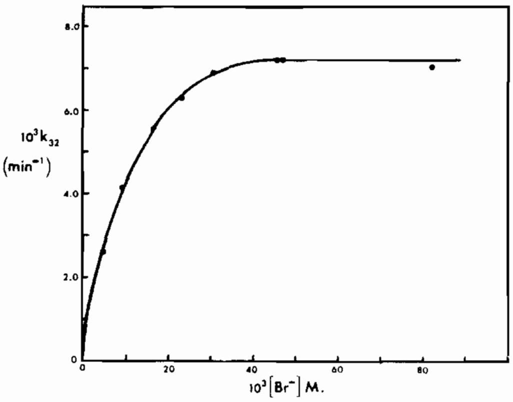

Figure 6. Variation of k_{32} with Uncomplexed Bromide Ion Concentration.

Rate constants for the anation of *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$, k_{32} only, by bromide ion are shown in Figure 6 as a function of bromide ion concentration at 40°. Complete retention was observed in anation ($k_{35}=0$). The isomerization of *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ could not be studied because the *trans* isomer, even at zero bromide concentration, was only 2% of the system.

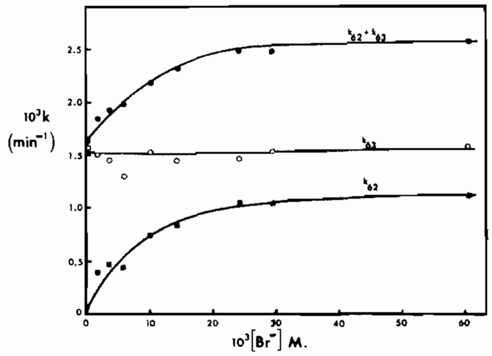

Figure 7. Variation of k_{62}, k_{63} and $(k_{62}+k_{63})$ with Uncomplexed Bromide Ion Concentration.

The rate constants for the isomerization (k_{63}) and anation (k_{62}) of *trans*–$[Cr(DMSO)_2(en)_2]^{3+}$ are shown in Figure 7. The products *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ and *cis*–$[CrBr(DMSO)(en)_2]^{2+}$ were formed in their equilibrium ratio. The values of both k_{63} and k_{62} are less precise than the other rate constants because of the relatively small change in absorption spectra found in these reactions.

Activation parameters for all the reactions followed are presented in Table III.

Discussion

(1) *Equilibria.* The equilibrium results for this system follow the trends established for other dianion-bisethylenediamine complexes of cobalt(III) and chromium(III) in dipolar aprotic solvents. It is now clear that for both chromium(III) and cobalt(III) complexes solvent containing complexes are most stable for dimethyl sulphoxide with decreasing relative stability through dimethylformamide (DMF), dimethylacetam-

ide (DMA) and sulfolane (TMS). DMSO, typical of oxygen donors forms more stable complexes with chromium(III) than cobalt(III) and bromide complexes are less stable to solvolysis by these solvents than the chloride containing analogues. In addition, as emphasized by solvent transfer activity coefficient data, the dipolar *cis* isomers have greater solution stability than the corresponding symmetrical *trans* isomers in strongly polar solvents.

It is thus not surprising that here we find the equilibria dominated by *cis* solvent containing species. It is not possible to extract an equilibrium constant for reaction (1) from the data in Figure 2 since, as previously established, the solution equilibria are dominated by successive ion association equilibria. Here it is seen that despite increases in free bromide ion concentration above $20\times10^{-3}\,M$, there is no increased anation at equilibrium. This can be shown not to be due to ion association of $(n\text{–}Bu)_4N^+Br^-$,[18] and thus must be relative stabilization of *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ as both ion pairs and ion triplets. At this point the bromide ion is more stable in the outer sphere of an inner sphere solvent containing complex than occupying an inner sphere site itself.

(2) *Kinetics.* (a) Solvolysis of *cis*–$[CrBr_2(en)_2]^+$. The results in Figure 4 are clearly not explicable in terms of a classical salt effect on a reaction involving a neutral species. The results are however quite similar to the bromide concentration dependence of the solvolysis rate of *cis*–$[CoBr_2(en)_2]^+$ in DMSO.[19] If as in the previous system the rate dependence is assigned to reactant ion association alone an ion association constant of $640\ l\ mol^{-1}$ at 50°C for the *cis*–$[CrBr_2(en)_2]^+Br^-$ is required which compares badly with the conductimetrically determined value of $61\ l\ mol^{-1}$ at 25°C, especially when it is remembered that the enthalpy of ion pairing in these systems is almost certainly negative.[8,20,21]

However we have emphasized[4,5,22,23] that the repercussions of ion association of the transition state is often dominant in these systems. If this is recognised and the system is formulated after Kurz as:[24,25]

$$\begin{tikzcd}
cis\text{–}[CrBr_2(en)_2]^+ + DMSO \arrow[r, shift left, "K^*"] \arrow[d, shift right, "+Br^-"'] & \text{TRANSITION STATE} \arrow[l, shift left] \arrow[r] \arrow[d, shift left] & \text{PRODUCTS} \\
cis\text{–}[CrBr_2(en)_2]^+ . Br^- + DMSO \arrow[r, shift left, "K'^*"] \arrow[u, shift right, "K_{IP}"'] & (\text{TRANSITION STATE } Br^-) \arrow[l, shift left] \arrow[r] \arrow[u, shift left, "K'"] & \text{PRODUCTS} + Br^-
\end{tikzcd}$$

where K* and K'* are the "equilibrium constants" for the formation of the free ion and ion paired transition states and where K' represents the formal equilibrium constant between the two transition states. It is assumed that no dynamic equilibrium exists between the transition states. K' will be given by $k_2/k_1\ K_{IP}$ where k_1 and k_2 are the rate constants for the free ion and ion paired solvolytic transition state. Using the value of $K_{IP} = 61\ l\ mol^{-1}$ at 25°C from conductivity measurements[8] the value of K' is calculated to be $36\ l\ mol^{-1}$ corresponding to a $\Delta G'$ of $-9.7\ kJ\ mol^{-1}$, a totally reasonable figure. The rate dependence shown in Figure 4 is then a superposition of ion association effects on both the reactant and transition state. It must be recognised that these two forms of reactant will normally lead to substantially different transiion states. Figure 8 shows the free energy profile consistent with these calculations and the activation parameters in Table III.

Here as with the cobalt(III) analogue the solvolysis occurs with retention irrespective of the ambient bromide ion concentration.

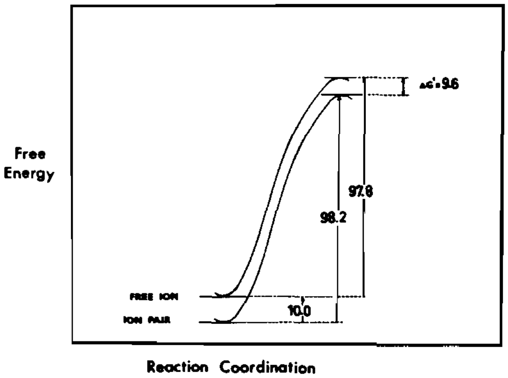

Figure 8. Reaction Co-ordinate Diagram for the Solvolysis of *cis*-$[CrBr_2(en)_2]^+$ in DMSO. Free Energy in kJ mol.$^{-1}$.

(b) Solvolysis of *trans*–$[CrBr_2(en)_2]^+$. The results in Table I clearly show that the rate of solvolysis of the *trans* isomer is free bromide concentration independent, and this despite the fact that reactions were studied in sufficiently high bromide concentrations to ensure a least 40% reactant ion association. This behaviour contrasts with the cobalt(III) analogue and suggests that in the present system the stabilization of the reactant by ion association is reflected in an almost identical transition state stabilization.

The steric course of this solvolysis also contrasts with the cobalt(III) system in that here we find 100% retention:

$$trans\text{–}[CrBr_2(en)_2]^+ + DMSO \rightarrow trans\text{–}[CrBr(DMSO)(en)_2]^{2+} + Br^-$$

in contrast to the total steric change found for *trans*–$[CoBr_2(en)_2]^+$. It has not been conclusively proven however that a very unstable *trans*–$[CoBr(DMSO)(en)_2]^{2+}$ species is not involved in the cobalt(III) system. The positive entropy of activation for *trans*–$[CoBr_2(en)_2]^+$ is consistent with systems giving with steric change and contrast with the negative value for the proven retention path of *trans*–$[CrBr_2(en)_2]^+$. These results for the DMSO solvolysis of both the *cis* and *trans* isocmers are similar to the aqueous hydrolysis reactions in respect to both the steric course and the absence of ethylenediamine loss.

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(25) J.L. Kurz and C.D. Gutsche, *ibid*, *82*, 2175 (1960).

(c) Reactions of *trans*–[CrBr(DMSO)$(en)_{22}$]$^{2+}$. Only one reaction, that of isomerization to *cis*–[CrBr(DMSO)$(en)_2$]$^{2+}$, was found for this substrate at all free bromide concentrations.

This isomerization rate was found to be independent of bromide concentration. In view of the dipositive charge and the small dipole moment possessed by this complex, an ion association constant in excess of 100 l mol^{-1} may be anticipated. Therefore in this reaction, stabilization by ion pairing of the reactant and the transition state appear to be coincidently equivalent. An approximately similar situation was observed for the isomerization of *cis*–[$CoBr_2(en)_2$]$^+$ in TMS[23] where the enthalpy of ion pairing for the reactant and transition state were both equal to –2.5 kJ mol^{-1}. Bosnich, Ferguson, and Tobe[26] found the rate of reaction of *trans*–[CoCl(CH_3OH)$(en)_2$]$^{2+}$ in methanol to be relatively independent of chloride concentration. They concluded that although ion association was complete within the range of chloride concentration studied, chloride ion in the inner solvation shell was "unable to compete effectively with methanol for the five coordinate intermediate when it was generated".

The isomerization of *trans*–[CrBr(DMSO)$(en)_2$]$^{2+}$ is almost certainly controlled by a solvent exchange step. The 100% conversion to the *cis* isomer would be difficult to explain in terms of loss of bromide ion being the rate determining step, especially at low bromide concentrations. This mechanism is further supported by the solvent exchange work of Lantzke and Watts[10,11] who found the rate of exchange of DMSO with *cis*–[CoCl(DMSO)$(en)_2$]$^{2+}$ was unaffected by ion pairing with bromide ion. However such a result, irrespective of mechanism, is not surprising when it is realized that loss or gain of a DMSO ligand does not alter the charge or significantly affect the dipole moment of the substrate and thus both the transition state and reactant would be similarly solvated and equally stabilized by ion pairing.

These results would fit equally well either an S_N1 or an S_N2 mechanism, although all associated work supports the dissociative mechanism. In an S_N1 mechanism, the stereochemical requirements for the formation of a trigonal bipyramid intermediate, as proposed by Basolo, Stone, and Pearson,[27] are such that a product ratio of 67% *cis* and 33% *trans*–[CrBr(DMSO)$(en)_2$]$^{2+}$ would be anticipated. Thus the observed isomerization rate would represent only 67% of the total rate of solvent exchange. A considerable amount of evidence for an S_N1 mechanism was compiled by Lantzke and Watts[11] when they calculated the theoretical spectrum of the *trans*–[CoCl(DMSO)$(en)_2$]$^{2+}$ and *trans*–[CoCl(DMF)$(en)_2$]$^{2+}$ ions in DMSO and DMF respectively, by assuming various product ratios for the reactions of the corresponding *cis* isomers in the appropriate solvent. The most reasonable spectra, which in fact compare very favourably with the spectra of the analogous chromium(III) complexes prepared in the course of the present study, were obtained by analysing the first-formed product to be an 83:17 ratio mixture of *cis*- and *trans*–[CoCl(SOL)$(en)_2$]$^{2+}$, where SOL represents either DMSO or DMF. This particular product ratio corresponds to an S_N1 process in which both possible intermediates represent equally available reaction paths.[11] Thus the law of microscopic reversibility dictates that the isomerization of the *trans* isomer must involve at least one of the pentacoordinated intermediates. It is interesting to note that if solvent entry is allowed at al edges of the trigonal bipyramid intermediate, excluding those occupied by ethylenediamine ligands, a *cis* to *trans* product ratio of 86:14 would result. Experimental precision is such that it would be very difficult to differentiate between the two product ratios.

Previous studies[12] of the corresponding aquo complex *trans*–[CrBr(H_2O)$(en)_2$]$^{2+}$ showed that the predominant reaction was isomerization (90%) with 10% solvolysis which gave *cis*–[Cr$(H_2O)_2(en)_2$]$^{3+}$. One other feature in common between the two systems is the complete absence of a path for solvolysis to the *trans*–[Cr$(DMSO)_2(en)_2$]$^{3+}$ species. For the aquo system, where some bromide loss occurs, there must be a second pentacoordinate intermediate.[12]

(d) Reactions of *cis*–[CrBr(DMSO)$(en)_2$]$^{2+}$. Solvolysis of *cis*–[CrBr(DMSO)$(en)_2$]$^{2+}$ gave *cis*- and *trans*–[Cr$(DMSO)_2(en)_2$]$^{3+}$ in their equilibrium ratio, although the rate of formation of the latter product was not directly measurable. This reaction is directly analogous to the aquation of *cis*–[CrBr(H_2O)-$(en)_2$]$^{2+}$ where 0-10% of the first formed product was *trans*–[Cr$(H_2O)_2(en)_2$]$^{3+}$ and the remainder was the corresponding *cis* isomer.[12] The results in Figure 5, suggest that the rate determining step for the solvolysis of *cis*–[CrBr(DMSO)$(en)_2$]$^{2+}$ involves dissociation of coordinated bromine followed by solvent entry which is inhibited by the presence of bromide ions in the first solvation shell of the substrate. In other words, bromide ion in the first solvation shell competes favourably with the solvent for entry into the five coordinate intermediate resulting in some bromide for bromide exchange and causing a reduction in the overall solvolysis rate. The mechanism is therefore typically S_N1IP. This argument assumes that the rate of bromide loss is reasonably independent of bromide concentration and that the rate of solvolysis of the free ion represents the "true" rate of bromide dissociation (*i.e.* 9.78×10^{-3} min^{-1} at 40°), thus excluding the low probability of bromide reentry. This is supported to some extent by the relative constancy of the activation energy with the addition of bromide ion (Table III). The minimum limiting rate of removal of *cis*–[CrBr(DMSO)$(en)_2$]$^{2+}$ is reached at a bromide concentration of approximately 48×10^{-3} *M* which is sufficiently high to indicate that the complex would be completely in the form of the ion triplet and thus the steric course of solvolysis is virtually independent of the outer sphere composition. No *trans*–[CrBr(DMSO)$(en)_2$]$^{2+}$ was detected during the entire reaction and this is consistent with the previously discussed kinetics of the reactions of *trans*–[CrBr(DMSO)$(en)_2$]$^{2+}$.

The large negative entropy of activation for k_{23}, shown in Table III, is compatible with a highly solvated transition state, brought about by an increase

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[26] B. Bosnich, J. Ferguson and M.L. Tobe, *J. Chem. Soc.*, A, 1636 (1966).

[27] F. Basolo, B.D. Stone and R.G. Pearson, *J. Amer. Chem. Soc. 75*, 819 (1953).

in charge due to the loss of a bromine ligand, and also with solvation of the dissociating bromide ion itself. In addition, the relatively low activation energy values for this reaction may be compared with the extremely low value obtained by Lantzke and Watts[28] for the comparable aquation of *cis*–$[CoCl(DMA)(en)_2]^{2+}$:

$$cis\text{–}[CoCl(DMA)(en)_2]^{2+} + H_2O = cis\text{–}[Co(H_2O)(DMA)(en)_2]^{3+} + Cl^-$$

(e) Reactions of *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$. Although a very small amount of isomerization of this complex was observed its rate could not be measured. The only appreciable reaction of the *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ ion was the anation by bromide ion which must involve the same intermediate as the solvolysis of *cis*–$[CrBr(DMSO)(en)_2]^{2+}$. As illustrated in Figure 6 the anation shows the anticipated effects of ion association[3-5] in that associated bromide ion competes effectively with the solvent as the extent of the ion aggregation is increased. This is typical of an S_N1IP mechanism. The maximum limiting rate of anation, attained at a bromide concentration of approximately 45×10^{-3} *M*, may be due to the complex being completely in the form of an ion triplet with the possibility of an ion quadruplet existing. It must be remembered that the concept of the formation of ion aggregates in solution does not necessarily limit the maximum size of the aggregate to the number of ions required to produce electrostatic neutrality. Hughes and Tobe[29] have in fact postulated the existence of a negatively charged aggregate, *trans*–$[Co(NO_2)(H_2O)(en)_2]^{2+}3Cl^-$, in acetone.

The high activation energy for the anation of *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ is in keeping with the high values obtained by Fitzgerald and Watts[30] for the anation of a series of similar cobalt(III) complexes in dipolar aprotic solvents. The large positive entropy of activation of 76 JK^{-1} mol^{-1} is consistent with the loss of solvent order which must exist for a highly charged cation in such a dipolar solvent. It must be remembered that the difference between an S_N1 and an S_N2 mechanism is rather a matter of timing of the bond breaking and bond making steps in the transition state. Although for a dissociative mechanism bond breaking is the initiating step, Cr–Br bond making may be sufficiently developed in the transition state to produce a considerable lowering of the solvation ordering. The advance of the anion entry step in a dissociative reaction is expected with increase in the positive charge of the reactant complex.

(f) Reactions of *trans*–$[Cr(DMSO)_2(en)_2]^{3+}$. The reactions of *trans*–$[Cr(DMSO)_2(en)_2]^{3+}$ are the most interesting of the reactions studied in this system. The isomerization and anation products, *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ and *cis*–$[CrBr(DMSO)(en)_2]^{2+}$ respectively, were formed directly in their equilibrium ratio at all stages in all runs conducted. In other words, the rate constants k_{23} and k_{32} are sufficiently small with respect to the rate constants k_{63} and k_{62} that the product composition is not controlled by secondary interconversions to give the final equilibrium composition. One must conclude that both reaction paths involve the same intermediate which logically may be assumed to be the intermediate independently encountered in the study of the reactions of the products (i.e. k_{23} and k_{32}). A common intermediate for all three species would be accounted for by a reaction profile diagram of the type shown in Figure 9. The discrepancy of 1.7kJ mol^{-1} between the free energy terms is well within the experimental error. A profile diagram of this type was proposed by Watts[4] for the dissociative isomerization and anation reaction of a series of analogous cobalt(III) complexes.

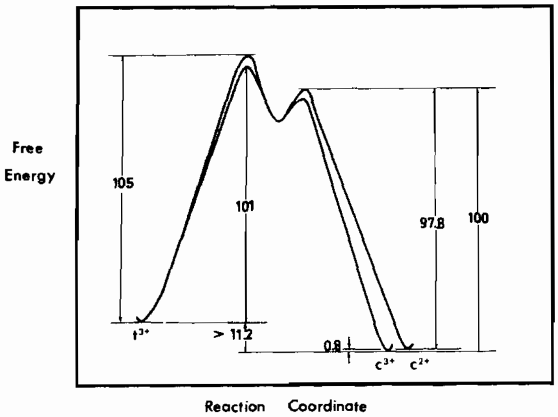

Figure 9. Reaction Co-ordinate Diagram for the Reaction of *trans*-$[Cr(DMSO)_2(en)_2]^{3+}$ (t^{3+}), *cis*-$[Cr(DMSO)_2(en)_2]^{3+}$ (c^{3+}), and *cis*-$[CrBr(DMSO)(en)_2]^{2+}$ (c^{2+}). Free Energies in kJ mol^{-1}.

As shown in Figure 7, the rate of isomerization, k_{63}, of *trans*–$[Cr(DMSO)_2(en)_2]^{3+}$ is independent of bromide concentration and indicates that isomerization and anation involve different transition states. For a dissociative mechanism an increase in the rate of anation would be expected to cause a decrease in the rate of isomerization assuming isomerization in the absence of bromide ion corresponds to the maximum rate of dissociative acts of the substrate less those acts which result in retention of configuration. As $k_{65} = O$, retention of configuration is equivalent to solvent exchange. However the rate of dissociation of cordinated DMSO cannot be assumed independent of bromide concentration since this neglects the affect of bromide ion on the transition states for isomerization and anation. In fact, the independence of k_{63} on the bromide concentration is analogous to rate of isomerization, k_{52}, of *trans*–$[CrBr(DMSO)(en)_2]^{2+}$ discussed previously. The alternative that isomerization of *trans*–$[Cr(DMSO)_2(en)_2]^{3+}$ occurs by *cis* attack through an associative mechanism is incompatible with the idea of a common intermediate for the isomerization and anation reactions.

The anation reaction involves a 100% change in configuration which implies some degree of preorientation of the nucleophilic bromide ion within the inner solvation shell of the substrate, and/or the intermediate, such that dissociation of a DMSO li-

[28] I.R. Lantzke and D.W. Watts, *Aust. J. Chem.*, 19, 1821 (1966).
[29] M.N. Hughes and M.L. Tobe, *J. Chem. Soc.*, 1204 (1965).
[30] W.R. Fitzgerald and D.W. Watts, *J. Amer. Chem. Soc.*, 90, 1734 (1968).

gand leads to only *cis* attack. Specific sites for interionic interaction are difficult to predict for the non-polar substrate but are likely to exist in the development of unsymmetrical five coordinate intermediates.

It is apparent that ion association is virtually complete (in view of the high charge on the cation, this may correspond to an ion triplet) at bromide concentrations of the order of 50×10^{-3} *M* where the observed product ratio is 3:2, *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ to *cis*–$[CrBr(DMSO)(en)_2]^{2+}$ with no *trans* anation product. Assuming a five cordinate intermediate of the type proposed by Basolo and Pearson[31] and shown in Figure 10a, a product ratio of 2:1 of *cis* to *trans* complex is predicted for solvent or anion entry along the three equatorial edges of the trigonal bipyramid. Since *trans*–$[CrBr(DMSO)(en)_2]^{2+}$ was not an observed product, no bromide entry can occur at the edge DC in Figure 10a. This is surprising as this *trans* position would appear to be a very favourable site for ion pairing. Perhaps this result emphasizes that, for a dissociative mechanism, the bond breaking step (i.e. in this case, the dissociation of a coordinated DMSO) need not be complete before bond making commences producing a slightly distorted trigonal bipyramid intermediate. The outgoing DMSO molecule effectively eliminates the edge DC as an active site for attack, at least for anation.

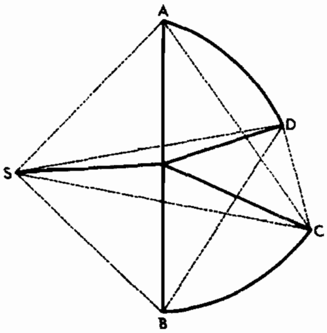

Figure 10A. Possible Reaction Intermediates.

If the favourable sites for anion association are along the other edges which are terminated by hydrogen bonding sites as has been suggested by n.m.r. studies[21] then the remaining edges for ion association will be AC and BD (Figure 10a). If entry of anions at these edges is of equal probability to solvent entry at the edges SA, SB, SC and SD then a 2:1 ratio of *cis*–$[Cr(DMSO)_2(en)_2]^{3+}$ to *cis*–$[CrBr(DMSO)(en)_2]^{2+}$ is predicted. The same consideration based upon the intermediate, Figure 10b predicts that this ratio is 3:2. Although these simple statistical considerations are unlikely to be valid in such electrostatically unsymmetrical intermediates they do confirm that the result are compatible with a dissociative intermediate of this type provided it is recognised that entry is advanced upon dissociation and that the outgoing group, in this case a DMSO molecule, can eliminate en entry site for anation.

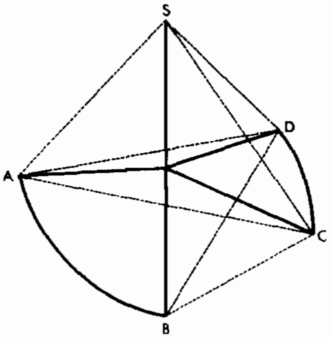

Figure 10B. Possible Reaction Intermediates.

Solvent exchange studies are clearly necessary for a more detailed elucidation of the mechanisms involved here. Kruse an Taube[32] have studied the isomerization and water exchange of *cis* and *trans*–$[Co(H_2O)_2(en)_2]^{3+}$. They observed each act of solvent exchange with the *trans* isomer brought about isomerization which is compatible with the results discussed earlier in that *trans* products are not observed. The *cis*–$[Co(H_2O)_2(en)_2]^{3+}$ isomer underwent water exchange at a rate approximately sixty five times the rate of isomerization and could only be explained in terms of a reaction path involving two intermediates. In the absence of DMSO exchange data this two intermediate scheme is indistinguishable from the single intermediate path proposed in Figure 9. Finally the authors suggested a second path existed in which cleavage of the Co–N bond with the ethylenediamine ligands occurred. This possibility certainly cannot be ignored in the system studied here, although it seems unlikely. The photochemical reactions of these complexes in DMSO, in which one end of the ethylenediamine is lost, strongly suggest that once cleavage of the Cr–N bond occurs it is not reformed, but rather further solvolysis occurs to give free ethylenediamine.[33]

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[31] F. Basolo and R.G. Pearson, « Mechanisms of Inorganic Reactions, » 1st. edition, John Wiley and Sons Inc., New York, 1958.

[32] W. Kruse and H. Taube, *J. Amer. Chem. Soc.*, *83*, 1280 (1961).

[33] A.W. Adamson and D.W. Watts, unpublished results.